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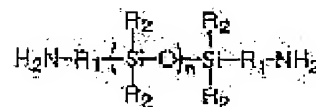
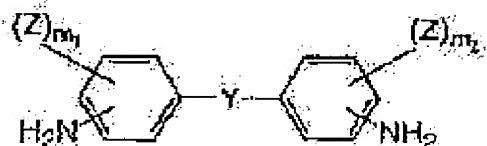
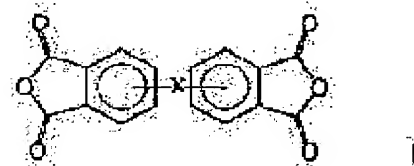
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(54) PHOTSENSITIVE POLYIMIDESILOXANE, COMPOSITION AND INSULATING FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject compound exhibiting excellent solubility in organic solvents and high photosensitivity, capable of forming cured films excellent in heat resistance and flexibility, and useful for electric insulating films, etc., by reacting a specific polyimidesiloxane with a (meth)acryloyl group-containing compound.

SOLUTION: This photosensitive polyimidesiloxane is soluble in organic solvents, and is obtained by subjecting (B) a (meth)acryloyl group-containing compound to an addition reaction or a condensation reaction to or with (A) a polyimidesiloxane obtained by polymerizing (A1) a compound of formula I (X is O, CO, a direct bond) with (A2) the same moles of a diamine comprising (A2') a compound of formula II [Y is O, CH₂, SO₂, a direct bond, etc.; Z is OH, COOH, SH; (m₁), (m₂) are each 1] and (A2'') compound of formula III [R₁ is a divalent hydrocarbon; R₂ is a 1-3C alkyl, phenyl; (n) is 3-50] e.g. in amounts of 5-80 mol.% and 95-20 mol.%, respectively, and subsequently converting the obtained polyamic acid to the polyimide.



* NOTICES *

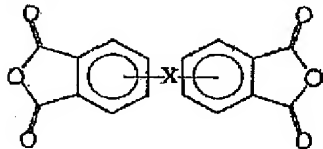
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CLAIMS

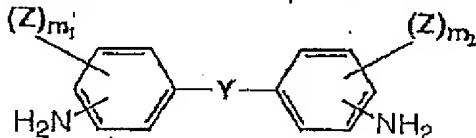
[Claim(s)]

[Claim 1] Aromatic tetracarboxylic dianhydride expressed with a following general formula, [Formula 1]



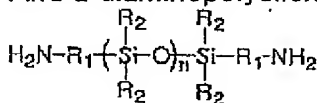
(However, X shows O, CO, or direct coupling among a formula.)

Aromatic diamine expressed with a following general formula, [Formula 2]



(However, Y shows O, CH₂, SO₂, or O-Bz-C(CH₃)₂-Bz-O or direct coupling among a formula, Z shows OH, COOH, or SH, and m₁ and m₂ are each 1.)

And a diaminopolysiloxane shown with a following general formula [Formula 3]



(However, among a formula, R₁ shows divalent hydrocarbon residue, and R₂ shows the alkyl group or phenyl group of the carbon numbers 1-3 independently, and) n shows the integer of 3-50. from — the compound which has an acryl group (meta-) in the poly imide siloxane with the becoming diamine which can obtain an equimolecular amount by polymerizing and imide-izing substantially — photosensitive poly imide siloxane of addition or the organic solvent fusibility which comes to carry out a condensation reaction.

[Claim 2] A photosensitive poly imide siloxane constituent which the photosensitive poly imide siloxane according to claim 1 dissolves in an organic solvent.

[Claim 3] Aromatic tetracarboxylic dianhydride, aromatic diamine, and a diaminopolysiloxane of many rings polymerize. It is an organic solvent solution of photosensitive poly imide siloxane which it was imide-ized and a photopolymerization nature unsaturation group content organic compound has combined with at least two benzene rings of an aromatic diamine component in polymer via a functional group. A photosensitive poly imide siloxane constituent in which development of an exposure film with an alkali developing solution is possible.

[Claim 4] The photosensitive poly imide siloxane constituent according to claim 2 or 3 which adds ten to inorganic bulking agent 100 detailed weight sections, such as mica, talc, barium sulfate, straw SUTONAITO, and calcium carbonate, to photosensitive poly imide siloxane 100 weight section.

[Claim 5] An insulator layer which carries out afterbaking and is developed by a case after applying a photosensitive poly imide siloxane constituent of a statement to a substrate and drying and exposing it by predetermined thickness in one paragraph of claims 2 thru/or 4.

[Claim 6] The insulator layer according to claim 5 in which exposure and an afterbaking film have an initial elastic modulus of 5-250 kg/cm², pyrolysis temperature of 300 to 450 **, and a volume resistance value of 5x10¹⁴-5x10¹⁵ omega-cm.

[Claim 7] An insulator layer of the heat resistance according to claim 5 which is the protective film of a circuit or a semiconductor device developed and provided, cold resistance, and electric insulation.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]

[Field of the Invention] the new aromatic poly imide siloxane which was excellent in solubility [as opposed to an organic solvent in this invention] and which contains a sensitization group in a polymers main chain — in detail, Excel in mechanical properties, such as heat resistance, electric, pliability, and Overcoat material and layer insulation material of a flexible wiring board, it is related with the photosensitive poly imide siloxane of organic solvent fusibility suitable as a formation material of the protective film of the circuit in semiconductor industry, the protective film of a semiconductor device, and a passivation film, etc., its organic solvent constituent, and an insulator layer.

[Description of the Prior Art] The overcoat material of a flexible wiring board, and the interlayer insulation film of a multilayer substrate, it is requested that layer insulation materials, such as an insulator layer to the solid state component in semiconductor industry, a formation material of a passivation film and an integrated circuit, and a multilayer printed wiring board, should be rich in heat resistance and insulation, and the existing photosensitive heat-resistant materials are called for from the demand of densification and high integration.

[0003] To these insulator layers, forming with heat-resistant high polyimide with insulation is proposed variously. However, each polymer which the thing using these polyimide generally does not have a sensitization group by solvent insolubility, or contains a sensitization group is a polyimide precursor, and it is necessary to carry out postbake of it at an after [photo-curing] elevated temperature, and to make it into POIMIDO. This brings about the heat deterioration of the substrate obtained.

[0004] Although there are also heat-resistant photorealist compositions (JP, 54-109828, A etc.) which mix the monomer which has a photorealist group to polyimide (it does not have a sensitization group) of organic solvent fusibility, and were made to carry out photo-curing to it, Such a constituent is inferior in a photorealist and, moreover, its heat resistance of polyimide after photo-curing is not enough, either.

[0005] Tetracarboxylic dianhydride and a diamine compound, for example, diamino CULCON, including an optical cross-linking unsaturated double bond are made to react, and obtaining polyimide excellent in photosensitivity and heat resistance is proposed (JP, 57-131227, A etc.). However, since the solubility over an organic solvent is inferior, the dissolution takes a long time, and although the polyimide produced by doing in this way is excellent in photosensitivity, when forming a relief pattern, there is a practical problem.

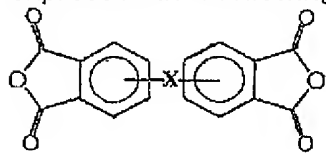
[0006] In order to obtain supple photosensitive polyimide, poly imide siloxane is proposed (JP, 2-50161, A.) Heating at high temperature is [since JP, 4-252227, A uses polyamic acid as a polymer component, in order that it may imide-size after patterning] required, and since a thermal damage is given to a substrate, there is a not desirable practical problem.

[0007] For this reason, in order to consider it as organic solvent soluble polyimide as one of the solution, Using diamine of the structure for un-of one core with the functional group which carries out the acrylate compound which has a reaction group like an epoxy group, for example (meta), and an addition reaction as aromatic diamine using tetracarboxylic dianhydride is performed. However, there was a problem that the stability of polymer liquid was inferior according to the solubility of polyimide not having an enough diamine component for one core.

[0008] [Problem(s) to be Solved by the Invention] The purpose of this invention is to provide the photosensitive polyimide which has high sensitivity and in which the solubility over an organic solvent is excellent, photo-curing is moreover carried out, and a photo-curing thing has high heat resistance and flexible nature. Other purposes of this invention are to provide the photosensitive solution composition which does not have a practical problem substantially. Other purposes of this invention are for the heating at high temperature (250-400 **) for being able to enlarge thickness and forming it into after-patterning imide to provide an unnecessary electrical insulation film.

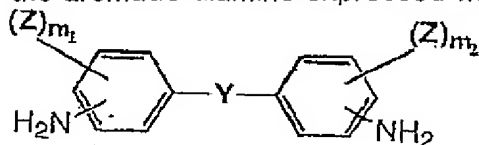
[0009] [Means for Solving the Problem] Namely, aromatic tetracarboxylic dianhydride as which this invention is

expressed in a following general formula, [Formula 4]

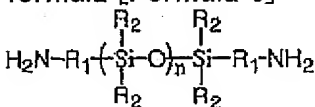


(However, X show O, CO, or direct coupling among a formula.)

the aromatic diamine expressed with a following general formula — and [Formula 5]



(However, Y among a formula O, CH₂, SO₂, or O-Bz-C(CH₃)₂-Bz-O or direct coupling) [show and] Z shows OH, COOH, or SH and m₁ and m₂ are 1 respectively. And diaminopolysiloxane shown with a following general formula [Formula 6]



(However, among a formula, R₁ shows divalent hydrocarbon residue, and R₂ shows an alkyl group or a phenyl group of the carbon numbers 1-3 independently, and) eta shows an integer of 3-50. from — a compound which has an acrylyl group (meta-) is related with poly imide siloxane with becoming diamine which can obtain an equimolecular amount by polymerizing and imide-izing substantially at addition or photosensitive poly imide siloxane of organic solvent fusibility which comes to carry out a condensation reaction.

[0009]This invention relates to a photosensitive poly imide siloxane constituent which the aforementioned photosensitive poly imide siloxane dissolves in an organic solvent.

[0010]In this invention, aromatic tetracarboxylic dianhydride, aromatic diamine, and a diaminopolysiloxane of many rings polymerize. It is an organic solvent solution of photosensitive poly imide siloxane which it was imide-ized and a photopolymerization nature unsaturation group content organic compound has combined with at least two benzene rings of an aromatic diamine component in polymer via a functional group. An exposure film is related with a photosensitive poly imide siloxane constituent in which development is possible with an alkali developing solution.

[0011]After this invention applies one of the aforementioned photosensitive poly imide siloxane constituents to a substrate and dries and exposes them by predetermined thickness, afterbaking of it is carried out and it relates to an insulator layer developed by a case.

[0012]Aromatic tetracarboxylic dianhydride of many rings photosensitive poly imide siloxanes of this invention are suitably indicated to be by said general formula. A substantial equimolecular amount with two kinds of diamine components of aromatic diamine and a diaminopolysiloxane which OH, COOH, or at least one SH combined at a time with the two benzene rings which have an amino group shown by said general formula. A compound which has an acrylyl group (meta) in poly imide siloxane which is random, or is obtained formation of heat imide or by making chemicals imide form in an organic solvent after carrying out block polymerization and considering it as polyamic acid can be manufactured addition or by carrying out a condensation reaction.

[0013]As aromatic tetracarboxylic dianhydride of many rings shown by said general formula in this invention, Biphenyl tetracarboxylic dianhydride, benzophenone tetra KARUPON acid dianhydride, An oxydi phthalic acid anhydride etc. are mentioned and 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 2,3,3',4'-biphenyl tetracarboxylic dianhydride (a-BPDA) can be mentioned suitably. A part of aromatic tetracarboxylic dianhydride of many rings may be replaced with aromatic tetracarboxylic dianhydride or aromatic dicarboxylic acid of one ring within limits which do not spoil solubility.

[0014]To the two benzene rings which have an amino group which is aromatic diamine shown by said general formula in this invention, independently OH, As aromatic diamine which COOH or one SH combined at a time, it is 3,3'-dihydroxy-4,4'-diaminobiphenyl, 4,4'-dihydroxy-3,3'-diaminobiphenyl, 5, and 5'-methylenebis, for example.

[2-aminobenzoic acid] The 4,4'-dihydroxy- 3, 3'-diaminodiphenyl ether, The 3,3'-dihydroxy- 4, 4'-diaminodiphenyl ether, A 3,3'-dihydroxy-4,4'-diamino diphenyl sulfide, 3,3'-dihydroxy-4,4'-diamino diphenyl sulfoxide, 3,3'-dihydroxy-4,4'-diaminodiphenyl sulfone, an 1,1-screw [4-(3-hydroxy-4-aminophenoxy) phenyl] Methane, 1,3-bis(3-hydroxy-4-aminophenoxy)benzene, a screw [4-(3-hydroxy-4-aminophenoxy) phenyl] A sulfone etc. can be mentioned, and this aromatic diamine may accept one sort, may be used, and may be used

combining two or more sorts. As the aforementioned aromatic diamine, it is 3,3'-dihydroxy-4,4'-diaminobiphenyl [from a viewpoint of the ease of receiving], 5, and 5'-methylenebis. [2-aminobenzoic acid] is used suitably. [0015] As a diaminopolysiloxane shown by said general formula in this invention, hydrocarbon residue divalent in R_1 in a general formula (3) — desirable — the carbon numbers 2-6 — it being especially "two or more methylene groups" or a phenylene group of the carbon numbers 3-5, and, it is preferred that R_2 is an alkyl group or phenyl groups of the carbon numbers 1-3, such as a methyl group, an ethyl group, and a propyl group, independently — further — 1 — 3-50 — it is preferably preferred 3-30, and that it is especially 5-20. The aforementioned diaminopolysiloxane may be a single compound as long as 1 is within the limits (3-50) of the above, and it may be a mixture of a compound in which 1 differs. As for 3-50, and it being especially within the limits of 5-20 also especially 3-30, and in it, when it is a mixture, 1 of average value calculated from amino equivalents is preferred. [0016] It is required to use aromatic diamine and said diaminopolysiloxane of said general formula as a diamine component in this invention. The aforementioned diaminopolysiloxane of aromatic diamine of an account of diamine component Nakamae is [the using rate / that it is / 80-30 mol / %] especially preferred 95-20-mol% 5-80-mol %, especially 20-70-mol%. When there are few rates of the aforementioned aromatic diamine, it is in a tendency for photosensitivity of photosensitive poly imide siloxane obtained to fall, and for resolution after photo-curing to become low, and for pyrolysis temperature of photosensitive poly imide siloxane to become low. When there are many rates of the aforementioned aromatic diamine, it is in a tendency for the organic solvent solubility of poly imide siloxane obtained to fall. [0017] Other aromatic diamine may be used together with the aforementioned aromatic diamine and a diaminopolysiloxane. As for the using rate, it is preferred that it is less than 30 mol % of a diamine component. As other aromatic diamine, for example 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl sulfone, Aromatic diamine which has the three benzene rings, such as aromatic diamine which has the two benzene rings, such as o-tolidine, 1,4-bis(4-aminophenoxy)benzene, and 1,4-bis(4-aminophenyl) benzene, or a screw [4-(4-aminophenoxy) phenyl] A sulfone, a 2,2-screw [4-(4-aminophenoxy) phenyl] Aromatic diamine which has the four benzene rings, such as propane, can be mentioned suitably. Although a rate of the aforementioned diamine component is determined from organic solvent solubility and photosensitivity (the ease of exposing), it is preferred to make it a rate which at least two photopolymerization nature unsaturation group content compounds have combined in a photosensitive poly imide siloxane molecule. [0018] Substantially photosensitive poly imide siloxane of this invention with an aromatic tetracarboxylic dianhydride ingredient a diamine component of an equimolecular amount, first, the inside of an organic solvent — reaction temperature of 100 ** or less, and random [desirable] with reaction temperature of 10-80 ** for about 1 to 48 hours or a block polymerization reaction — a random polymerization reaction being performed, and preferably, [rank second and] After diluting with an organic solvent a polyamic acid solution obtained by this polymerization reaction, temperature of 100 ** or less — desirable — reaction temperature of 10-50 ** — a chemicals imide-ized agent. For example, after adding imide-ized agents, such as tertiary amine like anhydrous carboxylic acid like an acetic anhydride, and pyridine, performing an imide-ized reaction for about 0.1 to 5 hours and considering it as poly imide siloxane, (Meta) It can obtain suitably by carrying out the addition reaction of the compound which has an acrylyl group. [0019] Or aromatic tetracarboxylic dianhydride and a diaminopolysiloxane, (Meta) Aromatic diamine which carries out an addition reaction to a compound which has an acrylyl group, substantial — equimolar, after adding a diaminopolysiloxane first like and making it react at 160-200 ** for about 1 to 5 hours, After adding said aromatic diamine, making it react with said reaction temperature for about 10 to 40 hours and compounding poly imide siloxane, photosensitive poly imide siloxane of this invention can be suitably obtained also by carrying out the addition reaction of the compound which has an acrylyl group (meta). [0020] A compound which has the aforementioned acrylyl group (meta) may be added to a poly imide siloxane solution after ending reaction directly (if required after cooling), or once isolating poly imide siloxane, it may add to a solution of an organic solvent used for a reaction, and an organic solvent which is the same or is different (or — the — it may be reverse). [0021] As a compound which has the aforementioned acrylyl group (meta), An organic compound which has a basis, meta-acryloyl, or an acrylyl group of OH(s), such as a glycidyl group and an isocyanate group, COOH, SH, addition, or condensation reaction nature, For example, glycidyl methacrylate, glycidyl acrylate, glycidyl polysiloxymethacrylate, half epoxy acrylate (for example, about five of about ten epoxy groups are the compounds replaced by an acrylate group.) For example, a trade name: Showa High Polymer make Vinyl-ester-resin RIPOKISHI 630X-501 etc. can be mentioned. [0022] As for the amount of compound used which has the aforementioned acrylyl group (meta), it is [more than this molar quantity] preferred that it is usually 1-10-mol twice to OH, COOH, or a sulfinyl group of aromatic diamine which OH, COOH, or one SH combined at a time with the benzene ring which has an amino group independently.

[0023]As an organic solvent in an addition reaction of a compound which has an above-mentioned polymerization reaction, an imide-ized reaction, and (meta) an acrylyl group, For example, N,N-dimethyl sulfoxide, N,N-dimethylformamide, a N,N-diethylformamide, N,N-dimethylacetamide, a N,N-diethylacetamide, N-methyl-2-pyrrolidone (NMP), hexamethylene phosphoamides, etc. are used.

[0024]Although a solution after ending reaction may be used as it is (after adding other additive agents if required), photosensitive poly imide siloxane of this invention may be used by a use as a solution which dissolved in an organic solvent what isolated, when using it, for example as a pattern formation material.

[0025]As the aforementioned organic solvent, sulfoxide series solvents, such as dimethyl sulfoxide and diethyl sulfoxide, Formamide system solvents, such as N,N-dimethylformamide and a N,N-diethylformamide, Acetamide series solvents, such as N,N-dimethylacetamide and a N,N-diethylacetamide, Pyrrolidone system solvents, such as N-methyl-2-pyrrolidone, an N-ethyl-2-pyrrolidone, and an N-vinyl-2-pyrrolidone, Glyme system solvents, such as a methyl jig lime and methyl TORIJI glyme, hexamethylphosphoric triamide, gamma-butyllactone, cyclohexanone, etc. can be mentioned.

[0026]As for a solution composition of photosensitive poly imide siloxane of this invention, it is preferred that solids concentration which is polymer is 20 to 50 % of the weight. In the aforementioned photosensitive poly imide siloxane solution, a sensitizer, a photopolymerization initiator, It is preferred to add an adhesive improving agent (for example, thermosetting resin, such as melamine resin), an oxygen interception agent (for example, vaseline, a wax, a surface-active agent), and an oxygen supplementary agent (for example, ascorbic acid, butyl phosphite). It is preferred to add a compound which can polymerize by light which has an ethylene nature unsaturation group in the range which does not spoil the physical properties of an insulator layer after photo-curing as a cross linking agent.

[0027]As an aforementioned sensitizer and a photopolymerization initiator, a Michler's ketone, benzoin, Benzoin methyl ether, benzoin ethyl ether, benzoin iso-propyl ether, 2-t-BICIRU anthraquinone, 1,2-benzo-9,10-anthraquinone, 4,4'-bis(diethylamino)benzophenone, an acetophenone, Benzophenone, a thioxan ton, a 1,5-acenaphthene, 1-hydroxy-cyclohexylphenyl ketone, The 2-benzyl-1,2-dimethylamino 1-(4-morpholinophenyl) butane- 1, 1-hydroxy-cyclohexylphenyl ketone, etc. can be mentioned, Especially the addition has two to 30 preferred weight section one to 50 weight section to poly imide siloxane 100 weight section in total.

[0028]As the aforementioned cross linking agent, ethylene glycol dimetha- (a) KURIRETO, Propylene glycol dimetha- (a) KURIRETO, trimethylolpropane TORIMETA (a) KURIRETO, Tetramethylolmethanetetra meta-(a) KURIRETO, N, and N'-methylenebis meta-(a) KURIRETO, diethylaminoethyl meta-(**) — chlorate and tris (hydroxyethyl acryloyl) isocyanurate. phosphoric acid meta-(**) — KURIRETO, polythiol (for example, trimethylolpropanetris thiopropionate), thiols (for example, CHIOGU reel acid), etc. can be raised. As for especially the addition, it is preferred to carry out 10-60 weight-section addition five to 100 weight section to photosensitive poly imide siloxane 100 weight section.

[0029]A solution composition of photosensitive poly imide siloxane of this invention, Aerosil (ten to 50 weight section of the amount used is preferred to photosensitive poly imide siloxane 100 weight section), Detailed inorganic bulking agents, such as mica, talc, barium sulfate, straw SUTONAITO, and calcium carbonate (the amount used) ten to 100 weight section is preferred to photosensitive poly imide siloxane 100 weight section — a detailed polymer filler — or it is detailed or inorganic matter of fusibility, or organic dye and paints may be made to contain And a solution composition makes colorlessness or Phthalocyanine Green, copper phthalocyanine blue, etc. contain, and may be colored.

[0030]Photosensitive poly imide siloxane of this invention can be used, and a pattern can be formed as follows with a photosensitive poly imide siloxane solution composition as mentioned above. That is, first, the above-mentioned photosensitive poly imide siloxane solution is applied to a substrate, it dries and an organic solvent is removed. Screen-stencil, a curtain roll, a reverse roll, etc. can perform spreading to a substrate. 90 ** or less of desiccation of a coating film (thickness: preferably 5-100 micrometers, especially 10-100 micrometers) is preferably performed at 40-80 **. A photo mask of a negative mold is put on a dry coating film after desiccation, and it irradiates with active light, such as ultraviolet rays, visible light, and an electron beam. Subsequently, a pattern made from poly imide siloxane can be obtained by probing a development, for example, an unexposed portion, with a developing solution using a shower or an ultrasonic wave. As for a hardening layer, it is preferred that thickness is about 2-50 micrometers. The aforementioned development NaOH, KOH, Na₂CO₃, A mixed solution with combination with solution occasion organic solvents, such as Na₂B₄O₇, organic alkali, for example, tetraethylammoniumhydroxide and water, or an organic solvent can be used as an alkali developing solution.

[0031]As an organic solvent of the above-mentioned developing solution, N,N-dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, N-methyl-2-pyrrolidone, Hexamethylene phosphoamides, a jig lime, Tori Gleim, ethylene glycol monoethyl ether, Organic solvents or these mixed liquor, such as ethylene glycol monobutyl ether, diethylene-glycol monobutyl ether, methanol, and ethanol, can be used.

[0032]Photosensitive poly imide siloxane of this invention has the outstanding solubility, therefore can remove poly imide siloxane of an unexposed portion easily, and, thereby, can form a pattern easily.

[0033]Photosensitive poly imide siloxane and a solution composition of this invention, Since it has high photosensitivity and excels in a light transmittance state and optical cross-linking, resist for image formation is not separately needed like conventional non-exposing polyimide, Heating at high temperature (250-400 **) for imide-izing after image formation is not needed like photosensitive polyamic acid, Since a 150-200 ** afterbaking process is enough, an effect which was excellent in many, such as it not only bringing about high-reliability and low cost, but not giving a thermal damage of a substrate, is done so. For this reason, a photosensitive poly imide siloxane constituent of this invention can be used conveniently for a negative pattern or a positive pattern.

[0034]A pattern which consists of a hardening layer formed from photosensitive poly imide siloxane of this invention or its solution composition is excellent in heat resistance, and electric and mechanical properties, and excellent in especially pliability. For example, an insulator layer of this invention is a thing of resolution up to at least 20 micrometers, especially about 10-50-micrometer resolution after photo-curing by various exposure means in thickness about 2-50 micrometers thick suitably. For this reason, especially an insulator layer of this invention is suitable as insulating materials, such as a high-density flexible substrate, BGA, and CSP. And exposure and an afterbaking film of this invention produced by doing in this way are insulator layers which have an initial elastic modulus of 5-250 kg/cm², pyrolysis temperature of 300 to 450 **, and a volume resistance value of 5×10^{14} - 5×10^{15} ohm-cm suitably.

[0035]Hereafter, the example of this invention is shown. In each following example, evaluation was performed as follows.

[0036](Physical-properties examination)

1. It took to a 100-ml measuring flask, and N-methyl-2-pyrrolidone was added, it dissolved [0.5g precise weighing of the viscosity photosensitive poly imide siloxane of polyimide was done, and], and logarithmic viscosity was measured by the method of timing the falling time of liquid at 30 ** using canon Fenske's viscosity meter.

[0037]2. Apply the solution which dissolved 20 g of the film production nature photosensitivity poly imide siloxane of photosensitive poly imide siloxane in 100 ml of N-methyl-2-pyrrolidone on a Teflon board (1.0 mm) so that the film of poly imide siloxane may be set to about 20 micrometers in thickness, and it dries for 60 minutes at 60 **. The high-pressure mercury-vapor lamp performed the exposure of two of 1J/cm², and also it heat-treated for 60 minutes at 160 **, and wound around the round bar of 1 mmphi, and bending and generating of the cracker were observed. What has O and a crack in the case where there is no generating of a crack was made into x.

[0038]3. 0.2 g of soluble poly imide siloxane to NMP of poly imide siloxane is added to 0.8 g of N-methyl-2-pyrrolidone, The solution state of poly imide siloxane was observed and ** and the case of being insoluble were evaluated [the case where the case where it dissolves within 1 hour is dissolved within O and one day] for the case of only O and swelling as x.

[0039]4. It measured using the pyrolysis temperature thermo gravity analyzer.

5. The dam which makes a spacer a photo-curing characterization polyimide film (the Ube Industries make, polyimide film YUPI REXX S) is formed, On copper foil (35 micrometers), the bar coating machine was used, ink was cast uniformly, and the following photosensitivity and the examination of resolution were presented about the dry membrane obtained by drying for 60 minutes at 60 **. It applied to copper foil with a photosensitivity of 35 micrometers so that dry membrane thickness might be set to about 25 micrometers, and it dried for 60 minutes at 60 **. The Mikasa, Inc mask alignment device (MA-10 type) is used. It exposed through the glass mask, and in the 2% solution of tetraethylammonium hydroxide, and methanol, ultrasonic immersion was carried out, negatives were developed, and it was considered as photosensitivity with the light exposure which can obtain the pattern of the 100-micrometer line & space of a 200-micrometer pitch.

[0041]7. Teflon spreading of the mechanical properties measurement photosensitivity poly imide siloxane solution composition is carried out, For 60 minutes, after desiccation, 1 J/cm² ultraviolet rays exposure and solution composition at 160 ** succeeding for 1 hour, the film was exfoliated at 60 **, the test piece was started in the shape of a dumbbell, and it measured according to ASTM D882 using the tension tester, and asked for tensile strength, the pace of expansion, and the initial elastic modulus.

[0042]8. A photosensitive poly imide siloxane solution composition is applied so that dry membrane thickness may be set to 80 micrometers on the copper plate of 0.3 mm of electric property measurement thickness. Based on JIS-C 2103 (the varnish examining method for electric insulation), it examined [at 60 **] after desiccation about 1J/cm² ultraviolet rays exposure and the sample succeedingly obtained by heating for 1 hour at 160 ** for 60 minutes, and the volume resistance value was measured.

9. Cold-resistant evaluation-65 ** estimated what a crack does not generate in an insulator layer at maintenance and 125 ** for 30 minutes after making 30-minute maintenance into one cycle and carrying out 200

cycles at -65 °C subsequently, 30-minute maintenance and that cold resistance is good, and what a crack generates was estimated that cold resistance is poor.

[0043]Add 17.494 g (0.059 mol) of example 1(poly imide siloxane synthesizing process)2,3,3',4'-biphenyl tetracarboxylic dianhydride (a-BPDA) to 54 g of N-methyl-2-pyrrolidone (NMP), and it dissolves, 36.540 g of diaminopolysiloxanes (R_1 = pro pull, R_2 = methyl, η = 10, amino-equivalents =450) were added, and it reacted at 180 °C for 2 hours. The 3,3'-dihydroxy-4,4'-diaminobiphenyl 3.740g (0.017 mol) was added successfully, and it reacted for 30 hours. Subsequently, at the temperature of 100 °C, added 9.893 g (0.070 mol) of glycidyl methacrylate, it was made to react for 0.5 hour, and photosensitive poly imide siloxane was obtained (as a solution).

[0044](Ink chemically-modified degree) NMP18g is added and diluted in the solution whole quantity of the above-mentioned photosensitive poly imide siloxane, 7.8 g of Aerosil (mean particle diameter: about 0.02 micrometer), 13.4 g of talc (mean particle diameter: 1.5 micrometers), 4.7 g of dimethylbenzoic acid ethyl, 2.4 g of diethylthio xantho, and 9.7 g of trimethylolpropane triacrylate were added as a photoinitiator, it kneaded with 3 rolls, and the ink:photosensitivity poly imide siloxane solution composition was obtained. The measurement result and evaluation result about this photosensitive poly imide siloxane solution composition are collectively shown in Table 1 and 2.

[0045]2.6 kg/cm² and elongation were [the initial elastic moduli of the mechanical properties of exposure and an afterbaking film of tensile strength] 102.9 kg/cm² 8.2%. The volume resistance value of the electric property measurement result of exposure and an afterbaking film was 2.2×10^{15} ohm-cm. The cold resistance of this insulator layer was also good.

[0046]It dissolves 17.139 g of example 2(poly imide siloxane synthesizing process)2,3,3',4'-biphenyl tetracarboxylic acid 2 anhydrous (a-BPDA) in 54.0 g of N-methyl-2-pyrrolidone, 36.540 g of diaminopolysiloxanes (it is the same as the above) were added, and it reacted at 180 °C for 2 hours. It is 5 and 5'-methylenebis successfully. [2-aminobenzoic acid] (MBAA) 4.593 g was added and it reacted for 2 hours. Subsequently, at the temperature of 100 °C, 9.894 g of glycidyl methacrylate was made to react for 0.5 hour, and the photosensitive poly imide siloxane solution was obtained.

[0047](Ink chemically-modified degree) It evaluated from the above-mentioned photosensitive poly imide siloxane by preparing a photosensitive poly imide siloxane solution composition like Example 1. The result about this photosensitive poly imide siloxane solution composition is collectively shown in Table 1 and 2.

[0048]1.62 kg/cm² and elongation were [the initial elastic moduli of the mechanical properties of exposure and an afterbaking film of tensile strength] 55.5 kg/cm² 7.7%. The volume resistance value of the electric property measurement result of exposure and an afterbaking film was 2.8×10^{15} ohm-cm. The cold resistance of this insulator layer was also good.

[0049]18.876 g of example 3(poly imide siloxane synthesizing process)3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) is dissolved in 54.0 g of N-methyl-2-pyrrolidone, 36.540 g of diaminopolysiloxanes (it is the same as the above) were added, and it reacted at 180 °C for 2 hours. 3.765 g of 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB) was added successfully, and it reacted for 2 hours. Subsequently, at the temperature of 100 °C, added 9.894 g of glycidyl methacrylate, it was made to react for 0.5 hour, and the photosensitive poly imide siloxane solution was obtained.

[0050](Ink chemically-modified degree) It evaluated from the above-mentioned photosensitive poly imide siloxane by preparing a photosensitive poly imide siloxane solution composition like Example 1. The result about this photosensitive poly imide siloxane solution composition is collectively shown in Table 1 and 2.

[0051]1.12 kg/cm² and elongation were [the initial elastic moduli of the mechanical properties of exposure and an afterbaking film of tensile strength] 75.5 kg/cm² 6.5%. The volume resistance value of the electric property measurement result of exposure and an afterbaking film was 1.8×10^{15} ohm-cm. The cold resistance of this insulator layer was also good.

[0052]In example 4 Example 1, replaced with talc, and mica was used, and also the appearance carried out, and the photosensitive poly imide siloxane solution composition was obtained. Similarly the result was good.

[0053]Although it was going to obtain photosensitive poly imide siloxane like Example 1 except not having used a comparative example 1 diamino siloxane, it is insoluble to N-methyl pyrrolidone in polymer, and the photo-curing characteristic was not able to be measured.

[0054]Except having replaced with comparative example 22,3,3',4'-biphenyl tetracarboxylic dianhydride, and having used pyromellitic dianhydride (PMDA), it carried out like Example 1 and photosensitive poly imide siloxane was obtained. It was only that the obtained photosensitive poly imide siloxane swells to N-methyl pyrrolidone, and ink liquid was not obtained and the photo-curing characteristic was not able to be measured.

[0055]Replaced with comparative example 33,3'-dihydroxy-4,4'-diaminobiphenyl, and 3,5-diaminobenzoic acid was used, and also it carried out like Example 1. The obtained photosensitive poly imide siloxane did not dissolve

[0056] The photosensitive poly imide siloxane solution composition obtained in Example 5 - 8 each example was used, coat material was formed by the following methods, and the film was evaluated. By screen-stencil (200-micron mesh), ink was applied on the copper circuit pattern formed on 75 micrometers in thickness, or a 50-micrometer polyimide film (YUPI REXX S). Subsequently, it dried at 60 ** for 1 hour, and the organic solvent was removed. The Mikasa, Inc Mikasa, Inc mask alignment device (it exposed through the glass mask using the MA-10 mold 9.) Ultrasonic immersion was carried out for 2 minutes in methanol after immersion for ultrasonic 2 minutes in the 2% solution of tetraethylammonium hydroxide, and the pattern was formed. Subsequently, afterbaking was carried out at 160 ** for 1 hour, and the insulator layer was obtained. The normal pattern was similarly obtained except having carried out using the 20% solution of 1% of sodium borate, and diethylene-glycol monobutyl ether as a developing solution.

[0057] When flexibility was investigated for flexibility using the bending-test machine of Shimadzu, the crack generated neither also 1mmph. As for neither, abnormalities were accepted, when product flux S made from SANWA chemicals-270 was applied to the surface, and solder heat resistance was immersed in 260 ** solder for 30 seconds and was investigated. When unelectrolyzed [-proof] tinning nature was immersed for 2 minutes in the unelectrolyzed tinning liquid made from SHIPURE (tempo JITTO FT-34) and was investigated at 70 ** in it, MOGURI of tinning liquid was substantially observed in neither. When curvature was applied so that dry membrane thickness might be set to 30 micrometers to a polyimide film (the Ube Industries make, YUPI REXX 75S), and it processed on the same conditions as solder heat resistance and generating of curvature was investigated, curvature was not seen substantially [all].

[0058] As photosensitive polymer of comparative example 4 marketing, it patterned like Example 5 by liquefied development type solder resist PSR-1000 made from solar ink. As a result, the crack occurred by the crookedness test in the round bar of 1 mmph. Electric insulation was 1.2×10^{13} omega-cm in the initial value.

[0059] Table 1
表 1

酸二無水物の種類	ジブミン	ジブミン
実施例 1	a-BPDA	ジブミン/ポリシロキサレン 70 3, 3'-ジヒドロキシ-4, 4'-ジブミン/ピフエニル 30
実施例 2	a-BPDA	ジブミン/ポリシロキサレン 70 3, 3'-ジヒドロキシ-4, 4'-ジブミン/ピフエニル 30
実施例 3	BTDA	ジブミン/ポリシロキサレン 70 5, 5'-メチレンビス (2-ブミン/安息香酸) 30
比較例 1	a-BPDA	— 100
比較例 2	PMDA	ジブミン/ポリシロキサレン 70 3, 3'-ジヒドロキシ-4, 4'-ジブミン/ピフエニル 30
比較例 3	a-BPDA	ジブミン/ポリシロキサレン 70 3, 5'-ジブミン/安息香酸 30

[0060] Table 2

	対数粘度	膜性	溶解性	熱分解温度 ℃	解像力 膜厚 μm	光感度 mJ/cm^2
実施例 1	0.25	○	◎	416	26	80
実施例 2	0.18	○	◎	408	25	50
実施例 3	0.29	○	○	405	28	100
比較例 1	—	—	×	—	—	—
比較例 2	—	—	×	—	—	—
比較例 3	—	—	△	—	—	—

[0061]Example 9 (poly imide siloxane synthesizing process) a-BPDA 34.94g was dissolved in Tori Gleim 100g, 65.006 g of diamino polish ROKIN (R_1 = propyl, R_2 = methyl, and amino-equivalents =467) was added, and it was made to react at 180 ** for 1 hour. Reacted [MBAA12.250g] for 20 hours at the temperature succeedingly, and subsequently added glycidyl methacrylate (acid component: diamine component =1.00:1.00) of the specified quantity at the temperature of 100 **, it was made to react for 0.5 hour, and photosensitive poly imide siloxane was obtained (as a solution).

[0062](Ink chemically-modified degree) As opposed to 100 copies (it is [a weight section and the following] the same) of polymerization liquid (53.7% of solids concentration) which is the above-mentioned photosensitive poly imide siloxane solution, adding 0.268 copy of Phthalocyanine Green and making it distribute -- the solution -- half epoxy acrylate (the Showa High Polymer Co., Ltd. make.) trade name: -- RIPOKISHI 630X-501 14.42 copy and polyethylene glycol dimethacrylate (the Aranaka village chemicals company make.) the phosphoric acid methacrylate (the Nippon Kayaku Co., Ltd. make.) which is a mixture of 1:1 of NK9G5.37 copy, dimethacryloyl oxy phosphate, and mono- methacryloyloxy phosphate Add, and continuously PM2 1.61 copy 2.74 copies of defoaming agents (the Dow Chemical Co. make, DB100), 14.67 copies of initiators (the Ciba-Geigy make, IRGACURE 184), and an initiator (the Ciba-Geigy make.) IRGACURE 369 7.33 copy, 5.87 copies of dimethylaminobenzoic acid ethyl ester, 0.27 copy of hydroquinone and 0.27 copy of methoxy hydroquinone next 16.1 copies of barium sulfate (mean particle diameter: 0.3 micrometer), and 5.37 copies of Aerosil (mean particle diameter: about 0.02 micrometer) are added as 2.93 copies of diethylthio xanthenes, and an antigelling agent, It kneaded with 3 rolls and the ink:photosensitivity poly imide siloxane constituent was obtained.

[0063]Coat material was formed as the conventional method from this ink, and when unelectrolyzed [-proof] tinning nature was immersed for 3 minutes in unelectrolyzed tinning liquid (the product made by SHIPURE, tempo JITTO FT-34) and was checked at 70 ** in it, diving of tinning liquid was not accepted substantially. Apply this ink to 35-micrometer-thick copper foil, and it dries for 60 minutes at 60 **, After dry membrane thickness is exposed with the photosensitivity of $100 \text{ mJ}/\text{cm}^2$ at 23 micrometers using the Mikasa, Inc Mikasa, Inc mask alignment device, In the 2% solution of tetraethylammonium hydroxide, and methanol, ultrasonic immersion was able to be carried out, negatives were able to be developed, and the pattern of the 100-micrometer line & space was able to be obtained. This exposure and afterbaking film showed good mechanical and thermal (it is [***** and the following] the same) / electric physical properties equivalent to Example 1.

[0064]In the polymerization liquid (53.7% of solids concentration) which is a photosensitive poly imide siloxane solution produced by making it be the same as that of example 10 (ink chemically-modified degree) Example 9. Replaced with phosphoric acid methacrylate, and 16.1 copies of melamine resin (SANWA chemical company make, NIKARAKKU MW-100LM) was added, and also it carried out like Example 9, and the ink:photosensitivity poly imide siloxane constituent was obtained.

[0065]Coat material was formed as the conventional method from this ink, and when unelectrolyzed [-proof] tinning nature was immersed for 3 minutes in unelectrolyzed tinning liquid (the product made by SHIPURE, tempo JITTO FT-34) and was checked at 70 ** in it, diving of tinning liquid was not accepted substantially. Apply this ink to 35-micrometer-thick copper foil, and it dries for 60 minutes at 60 **, After dry membrane thickness is exposed with the photosensitivity of $100 \text{ mJ}/\text{cm}^2$ at 23 micrometers using the Mikasa, Inc Mikasa, Inc mask alignment device, In the 2% solution of tetraethylammonium hydroxide, and methanol, ultrasonic immersion was able to be carried out, negatives were able to be developed, and the pattern of the 100-micrometer line & space was able to be obtained. This exposure and afterbaking film showed good mechanical and thermal / electric physical properties equivalent to Example 1.

[0066]Example 11 (ink chemically-modified degree) phosphoric-acid methacrylate was not added, but replaced

with 16.1 copies of barium sulfate, and 16.1 copies of calcium carbonate (mean particle diameter: 1.2 micrometers) was used, and also it carried out like Example 9, and the ink:photosensitivity poly imide siloxane constituent was obtained.

[0067]Apply this ink to 35-micrometer-thick copper foil, and it dries for 60 minutes at 60 **, After dry

membrane thickness is exposed with the photosensitivity of 100 mJ/cm² at 23 micrometers using the Mikasa, Inc Mikasa, Inc mask alignment device, In the 2% solution of tetraethylammonium hydroxide, and methanol,

ultrasonic immersion was able to be carried out, negatives were able to be developed, and the pattern of the 100-micrometer line & space was able to be obtained. This exposure and afterbaking film showed good

mechanical and thermal / electric physical properties equivalent to Example 1.

[0068]Did not add example 12 (ink chemically-modified degree) phosphoric-acid methacrylate, but after adding a deforming agent, 2.68 copies of white vaseline (made by Wako Pure Chem) were added further, and also it

carried out like Example 9, and the ink:photosensitivity poly imide siloxane constituent was obtained.

[0069]This ink paint film was dried separately, and a mask and 150 micrometers of film surfaces were able to be detached, it was able to expose with the photosensitivity of 1 J/cm², negatives were able to be developed as the conventional method, and the pattern of the 100-micrometer line & space of a 200-micrometer pitch was

able to be obtained. This exposure and afterbaking film showed good mechanical and thermal / electric physical properties equivalent to Example 1.

[0070]Did not add example 13 (ink chemically-modified degree) phosphoric-acid methacrylate, but after adding a deforming agent, 2.68 copies of ascorbic acid (made by Wako Pure Chem) was added further, and also it carried

out like Example 9, and the ink:photosensitivity poly imide siloxane constituent was obtained.

[0071]This ink paint film was dried separately, and a mask and 150 micrometers of film surfaces were able to be detached, it was able to expose with the photosensitivity of 1 J/cm², negatives were able to be developed as the conventional method, and the pattern of the 100-micrometer line & space of a 200-micrometer pitch was

able to be obtained. This exposure and afterbaking film showed good mechanical and thermal / electric physical properties equivalent to Example 1.

[0072]

[Effect of the Invention]The photosensitive poly imide siloxane of this invention has the outstanding solubility. Therefore, the poly imide siloxane of an unexposed portion is easily removable with a developing solution, for

example, an alkali developing solution.

[0073]The photosensitive poly imide siloxane of this invention has high photosensitivity. The resolution which is the photosensitivity thickness shows the sensitization characteristic is not less than 20 micrometers, a 100micromL/S formation light dose is below 100 mJ/cm², and the photosensitive poly imide siloxane constituent

of this invention has good photosensitivity.

[0074]Not less than (300 to 450 **) 300 ** of heat resistance which evaluated by pyrolysis temperature the insulator layer which is a hardening layer formed from the constituent of the photosensitive poly imide siloxane

of this invention is especially not less than 350 **.

Heat resistance and cold resistance are good.

[0075]It excels in a mechanical property, the electric insulation evaluated by volume resistance is superior to an epoxy resin, and a bending crack does not occur, but the hardening layer formed from the constituent of the photosensitive poly imide siloxane of this invention is excellent in flexible nature.

[Translation done.]

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(54) 【発明の名称】 感光性ポリイミドシロキサン、組成物および絶縁膜

(57) 【要約】

【課題】 光硬化特性および有機溶媒に対する溶解性に優れ、高温加熱が不要で、硬化膜の電気的性質および機械的性質が良好な感光性ポリイミドシロキサンを提供する。

【解決手段】 多環芳香族テトラカルボン酸二無水物と、芳香族ジアミンおよびジアミノポリシロキサンとからなるポリイミドシロキサンのベンゼン環に少なくとも2個の不飽和基含有有機化合物が芳香族ジアミンと官能基を介して結合してなる感光性ポリイミドシロキサンに関する。

ポリイミドシロキサン組成物。

【請求項5】 請求項2乃至4のいずれかの項に記載の感光性ポリイミドシロキサン組成物を所定の厚さで基材に塗布し、乾燥、露光した後、後加熱し、場合により現像してなる絶縁膜。

【請求項6】 露光・後加熱膜が、5-250kg/cm²の初期弾性率、300-450℃の熱分解温度、5×10⁻⁴-5×10⁻⁵Ω・cmの体積抵抗値を有する請求項5記載の絶縁膜。

【請求項7】 現像して設けられた、回路または半導体素子の保護膜である請求項5記載の耐熱性、耐寒性、電気絶縁性の絶縁膜。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 この発明は、有機溶媒に対する溶解性の優れた、高分子主鎖中に感光基を含有する新規な芳香族ポリイミドシロキサン、詳しくは、耐熱性、電気的および柔軟性等の機械的性質に優れ、フレキシブル配線板のオーバーコート材や層間絶縁材料、半導体工業における回路の保護膜や半導体素子の保護膜、パッシベーション膜の形成材料等として好適な有機溶媒可溶性の感光性ポリイミドシロキサン、その有機溶媒組成物、および絶縁膜に関するものである。

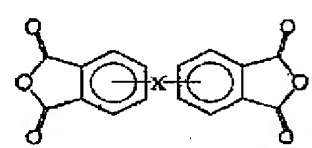
【0002】

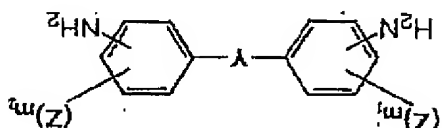
【従来の技術】 フレキシブル配線板のオーバーコート材や、多層基板の層間絶縁膜、また半導体工業における固体系子への絶縁膜やパッシベーション膜の形成材料、および半導体集積回路や多層プリント配線板などの層間絶縁材料は、耐熱性および絶縁性に富むことが要求され、また、高密度化、高集積化の要求から感光性のある耐熱材料が求められる。

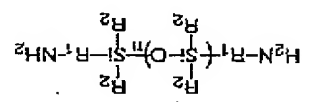
【0003】 これらの絶縁膜に対しては絶縁性とともに、耐熱性の高いポリイミドで形成することが種々提案されている。しかし、一般にこれらのポリイミドを用いたものは、溶媒不溶性で感光基を有していないか、感光基を含有するポリイミドは、いずれもポリイミド前駆体であり光硬化後高温でボストレークしてポリイミドとする必要がある。このことは、得られる基材の熱劣化をもたらす。

【0004】 また、有機溶媒可溶性のポリイミド（感光基を有しない）に、光硬化性基を有する単量体を混合し、光硬化させるようにした耐熱性フオトレジスト組成物のような組成物は、光硬化性が劣り、しかも光硬化後のポリイミドの耐熱性も充分ではない。

【0005】 また、フトラカルボネ酸二無水物と光架橋性不飽和二重結合を含むジエチン化合物、例えばジエチンアルコールとを反応させて、感光性および耐熱性に優れたポリイミドを得ることが提案されている（特開昭57-131227号公報等）。しかし、このようにして得

【特許請求の範囲】
【請求項1】 下記一般式で表される芳香族フトラカルボネ酸二無水物と、
【化1】


（ただし、式中、XはO、COまたは直接結合を示す。）
下記一般式で表される芳香族ジエチン、
【化2】


（ただし、式中、YはO、CH₂、SO₂またはO-BZ-C(CH₃)₂-BZ-Oまたは直接結合を示し、ZはOH、COOH又はSHを示し、m₁およびm₂は各々1である。）
および下記一般式で示されるジエチンポリシロキサン
【化3】


（ただし、式中、R₁は2価の炭化水素残基を示し、R₂は独立に炭素数1〜3のアルキル基またはフェニル基を示し、nは3〜50の整数を示す。）からなるジエチンとの実質的に等モル量を重合およびイミド化して得られるポリイミドシロキサンに、（メタ）アクリロイル基を有する化合物を付加または縮合反応させてなる有機溶媒可溶性の感光性ポリイミドシロキサン。
【請求項2】 請求項1記載の感光性ポリイミドシロキサンが有機溶媒に溶解してなる感光性ポリイミドシロキサン組成物。

【請求項3】 多環の芳香族フトラカルボネ酸二無水物、芳香族ジエチンおよびジエチンポリシロキサンが重合、イミド化され、かつポリマー中の芳香族ジエチン成分の少なくとも2個のベンゼン環に官能基を介して光重合性不飽和基含有有機化合物が結合している感光性ポリイミドシロキサンの有機溶媒溶液であって、露光膜がアルカリ現像液で現像可能な感光性ポリイミドシロキサン組成物。

【請求項4】 感光性ポリイミドシロキサン100重量部に対してマイカ、タルク、硫酸バリウム、フラストナイト、炭酸カルシウムなどの微細な無機充填剤10-100重量部を加えてなる請求項2または3記載の感光性

られるポリイミドは、感光性に優れているが、有機溶媒に対する溶解性が劣るため、溶解に長時間を要し、レリーフパターンを形成する上で実用上の問題がある。

【0006】また、柔軟性のある感光性ポリイミドを得るために、ポリイミドシロキサンが提案されている（特開平2-50161号公報、特開平4-252227号公報）が、ポリマー成分としてボリアミック酸を用いているためイミド化するためにパターンニング後、高温加熱が必要であり、基板に熱的ダメージを与えるので好ましくないなどの実用上の問題がある。

【0007】このため、解決策の一つとして、有機溶媒可溶性ポリイミドとするために、テトラカルボン酸二無水物を用い、芳香族ジアミンとして、例えばエポキシ基のような反応基を有する（メタ）アクリレート化合物と付加反応をする官能基を持った1核の非対象構造のジアミンを用いることが行われている。しかし、ジアミン成分が1核のためにポリイミドの溶解性が充分でないことによりポリマー液の安定性が劣るという問題があった。

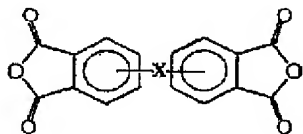
【0008】

【発明が解決しようとする課題】この発明の目的は、有機溶媒に対する溶解性が優れており、しかも光硬化して高い感度を有し、かつ光硬化物が高い耐熱性とフレキシブル性を有する感光性ポリイミドを提供することである。また、この発明の他の目的は、実用上の問題点を実質的に有しない感光性溶液組成物を提供することである。さらに、この発明の他の目的は、厚みを大きくでき、パターンニング後イミド化するための高温加熱（250～400℃）が不要の電気絶縁膜を提供することである。

【0009】

【課題を解決するための手段】すなわち、この発明は、下記一般式で表される芳香族テトラカルボン酸二無水物と、

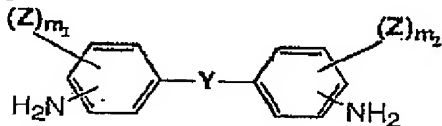
【化4】



（ただし、式中、XはO、COまたは直接結合を示す。）

下記一般式で表される芳香族ジアミンおよび

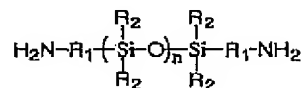
【化5】



（ただし、式中、YはO、CH₂、SO₂またはO-Bz-C(CH₃)₂-Bz-Oまたは直接結合を示し、

ZはOH、COOH又はSHを示し、m₁ およびm₂ は各々1である。）および下記一般式で示されるジアミノポリシロキサン

【化6】



（ただし、式中、R₁ は2価の炭化水素残基を示し、R₂ は独立に炭素数1～3のアルキル基またはフェニル基を示し、nは3～50の整数を示す。）からなるジアミンとの実質的に等モル量を重合およびイミド化して得られるポリイミドシロキサンに、（メタ）アクリロイル基を有する化合物を付加または縮合反応させてなる有機溶媒可溶性の感光性ポリイミドシロキサンに関するものである。

【0009】また、この発明は、前記の感光性ポリイミドシロキサンが有機溶媒に溶解してなる感光性ポリイミドシロキサン組成物に関するものである。

【0010】また、この発明は、多環の芳香族テトラカルボン酸二無水物、芳香族ジアミンおよびジアミノポリシロキサンが重合、イミド化され、かつポリマー中の芳香族ジアミン成分の少なくとも2個のベンゼン環に官能基を介して光重合性不飽和基含有有機化合物が結合している感光性ポリイミドシロキサンの有機溶媒溶液であって、露光膜がアルカリ現像液で現像可能な感光性ポリイミドシロキサン組成物に関する。

【0011】また、この発明は、前記のいずれかの感光性ポリイミドシロキサン組成物を所定の厚さで基材に塗布し、乾燥、露光した後、後加熱し、場合により現像してなる絶縁膜に関する。

【0012】この発明の感光性ポリイミドシロキサンは、好適には前記一般式で示される多環の芳香族テトラカルボン酸二無水物と、前記一般式で示されるアミノ基を有する2つのベンゼン環にOH、COOHまたはSHが最低1個ずつ結合した芳香族ジアミンとジアミノポリシロキサンとの二種類のジアミン成分との実質的等モル量を、有機溶媒中でランダムあるいはブロック重合させてボリアミック酸とした後、熱イミド化または化学イミド化させることにより得られるポリイミドシロキサンに、（メタ）アクリロイル基を有する化合物を付加または縮合反応させることによって製造することができる。

【0013】この発明における前記一般式で示される多環の芳香族テトラカルボン二無水物としては、ビフェニルテトラカルボン酸二無水物、ベンゾフェノンテトラカルボン酸二無水物、オキシジフタル酸無水物などが挙げられ、好適には3, 3', 4, 4'-ベンゾフェノンテトラカルボン酸二無水物、2, 3, 3', 4'-ビフェニルテトラカルボン酸二無水物（a-BPDA）を挙げることができる。溶解性を損なわない範囲内で多環の芳

【0021】前記の(メタ)アクリロイル基を有する化合物としては、グリシジル基、イソシアネート基などのOH、COOH、SHと付加あるいは縮合反応性の基とメタアクリロイルまたはアクリロイル基とを有する有機化合物、例えばグリシジルメタクリレート、グリシジルアクリレート、グリシジルポリシロキシメタアクリレート、ハーフエポキシアクリレート(例えば10個程度のエポキシ基のうち5個程度がアクリレート基で置換されている化合物である。例えば、商品名：昭和高分子製ビニルエステル樹脂リポキシ630X-501)などを挙げるができる。

【0022】前記の(メタ)アクリロイル基を有する化合物の使用量は、アミノ基を有するベンゼン環に別々にOH、COOH又はSHが1個ずつ結合した芳香族ジアミンのOH、COOH又はSH基に対して当モル量以上、通常は1~10モル倍であることが好ましい。

【0023】上記の重合反応、イミド化反応および(メタ)アクリロイル基を有する化合物の付加反応における有機溶媒としては、例えばN、N-ジメチルスルホキシド、N、N-ジメチルホルムアミド、N、N-ジエチルホルムアミド、N、N-ジメチルアセトアミド、N、N-ジエチルアセトアミド、N-メチル-2-ピロリドン(NMP)、ヘキサメチレンホスホアミドなどが用いられる。

【0024】この発明の感光性ポリイミドシロキサンは、反応終了後の溶液をそのまま(必要であれば他の添加剤を加えた後)使用してもよいが、用途によって、例えばパターン形成材料として使用する場合には、単離したものを有機溶媒に溶解した溶液として使用してもよい。

【0025】前記の有機溶媒としては、ジメチルスルホキシド、ジエチルスルホキシドなどのスルホキシド系溶媒、N、N-ジメチルホルムアミド、N、N-ジエチルホルムアミドなどのホルムアミド系溶媒、N、N-ジメチルアセトアミド、N、N-ジエチルアセトアミドなどのアセトアミド系溶媒、N-メチル-2-ピロリドン、N-エチル-2-ピロリドン、N-ビニル-2-ピロリドンなどのピロリドン系溶媒、メチルジグリム、メチルトリグリムなどのグリム系溶媒、ヘキサメチルホスホリックトリアミド、γ-ブチラクトン、シクロヘキサノンなどを挙げるができる。

【0026】この発明の感光性ポリイミドシロキサンの溶液組成物は、ポリマーである固形分濃度が20~50重量%であることが好ましい。前記の感光性ポリイミドシロキサン溶液に、増感剤、光重合開始剤、接着性改良剤(例えばメラミン樹脂などの熱硬化性樹脂)、酸素遮断剤(例えばワセリン、ワックス、界面活性剤)、酸素補足剤(例えばアスコルビン酸、ブチルフォスファイト)を添加することが好ましい。また、光硬化後の絶縁膜の物性を損なわない範囲でエチレン性不飽和基を有す

る光により重合可能な化合物を架橋剤として添加することが好ましい。

【0027】前記の増感剤および光重合開始剤としては、ミヒラーケトン、ベンゾイン、ベンゾインメチルエーテル、ベンゾインエチルエーテル、ベンゾインイソプロピルエーテル、2-tert-ブチルアントラキノン、1,2-ベンゾ-9,10-アントラキノン、4,4'-ビス(ジエチルアミノ)ベンゾフェノン、アセトフェノン、ベンゾフェノン、チオキサントン、1,5-アセナフテン、1-ヒドロキシ-シクロヘキシルフェニルケトン、2-ベンジル-1,2-ジメチルアミノ-1-(4-モルホリノフェニル)ブタン-1,1-ヒドロキシ-シクロヘキシルフェニルケトンなどを挙げるができる。その添加量は合計でポリイミドシロキサン100重量部に対して1~50重量部、特に2~30重量部が好ましい。

【0028】前記の架橋剤としては、エチレングリコールジメタ(ア)クリレート、プロピレングリコールジメタ(ア)クリレート、トリメチロールプロパントリメタ(ア)クリレート、テトラメチロールメタンテトラメタ(ア)クリレート、N、N'-メチレンビスメタ(ア)クリレート、ジエチルアミノエチルメタ(ア)クロレート、トリス(ヒドロキシエチルアクリロイル)イソシアヌレート、リン酸メタ(ア)クリレート、ポリチオール(例えばトリメチロールプロパントリスチオプロピオネート)、チオール類(例えばチオグリール酸)などをあげることができる。その添加量は感光性ポリイミドシロキサン100重量部に対して、5~100重量部、特に10~60重量部添加することが好ましい。

【0029】また、この発明の感光性ポリイミドシロキサンの溶液組成物は、アエロジル(使用量は、感光性ポリイミドシロキサン100重量部に対して10~50重量部が好ましい)、マイカ、タルク、硫酸バリウム、ワラストナイト、炭酸カルシウムなどの微細な無機充填剤(使用量は、感光性ポリイミドシロキサン100重量部に対して10~100重量部が好ましい)、微細なポリマー充填剤、あるいは微細なあるいは可溶性の無機あるいは有機染料・顔料を含有させてもよい。そして溶液組成物は無色あるいはフタロシアニングリーン、フタロシアニンブルーなどを含有させて着色してもよい。

【0030】この発明の感光性ポリイミドシロキサンを使用し、上記のようにして感光性ポリイミドシロキサン溶液組成物によって、以下のようにしてパターンを形成することができる。すなわち、先ず上記の感光性ポリイミドシロキサン溶液を基板に塗布し、乾燥して有機溶媒を除去する。基板への塗布はスクリーン印刷、カーテンロール、リバースロール等により行うことができる。塗布膜(好ましくは厚み：5~100μm、特に10~100μm)の乾燥は90℃以下、好ましくは40~80℃で行う。乾燥後、乾燥塗布膜にネガ型のフォトマスク

0. 3mm厚の銅板上に乾燥膜厚が $80\mu\text{m}$ となるように感光性ポリイミドシロキサン溶液組成物を塗布し、 60°C で60分間乾燥後、 $1\text{J}/\text{cm}^2$ 紫外線露光、引き続き 160°C で1時間加熱して得たサンプルについてJIS-C 2103（電気絶縁用ワニス試験法）に基づき試験を行って、体積抵抗値を測定した。

9. 耐寒性評価

— 65°C で30分保持、 125°C で30分保持、次いで— 65°C で30分保持を1サイクルとして、200サイクルした後に絶縁膜にクラックが発生しないものを耐寒性が良好と評価し、クラックが発生するものを耐寒性が不良と評価した。

【0043】実施例1

（ポリイミドシロキサン合成工程）2, 3, 3', 4'-ビフェニルテトラカルボン酸二無水物（a-BPD A）17.494g（0.059モル）をN-メチル-2-ピロリドン（NMP）54gに加えて溶解し、ジアミノポリシロキサン（ R_1 =プロプル、 R_2 =メチル、 $\eta=10$ 、アミノ当量=450）36.540gを加え 180°C で2時間反応した。引き続き3, 3'-ジヒドロキシ-4, 4'-ジアミノビフェニル3.740g（0.017モル）を加え30時間反応した。次いで温度 100°C にて、グリシジルメタクリレート9.893g（0.070モル）を加え0.5時間反応させて感光性ポリイミドシロキサンを得た（溶液として）。

【0044】（インキ化工程）上記の感光性ポリイミドシロキサンの溶液全量にNMP18gを加えて希釈し、アエロジル（平均粒径：約 $0.02\mu\text{m}$ ）7.8g、タルク（平均粒径： $1.5\mu\text{m}$ ）13.4g、光開始剤としてジメチル安息香酸エチル4.7g、ジエチルチオキサント2.4g、トリメチロールプロパントリアクリレート9.7gを添加し、3本ロールにて混練りしてインキ：感光性ポリイミドシロキサン溶液組成物を得た。この感光性ポリイミドシロキサン溶液組成物についての測定結果および評価結果をまとめて表1および表2に示す。

【0045】また、露光・後加熱膜の機械的物性は、引張強度が $2.6\text{kg}/\text{cm}^2$ 、伸びが8.2%、初期弾性率が $102.9\text{kg}/\text{cm}^2$ であった。また、露光・後加熱膜の電気物性測定結果は体積抵抗値が $2.2 \times 10^{15}\Omega \cdot \text{cm}$ であった。この絶縁膜は耐寒性も良好であった。

【0046】実施例2

（ポリイミドシロキサン合成工程）2, 3, 3', 4'-ビフェニルテトラカルボン酸二無水（a-BPDA）17.139gをN-メチル-2-ピロリドン54.0gに溶解し、ジアミノポリシロキサン（前記と同じ）36.540gを加え 180°C で2時間反応した。引き続き5, 5'-メチレンビス〔2-アミノ安息香酸〕（MBAA）4.593gを加え2時間反応した。次いで温

度 100°C にて、グリシジルメタクリレート9.894gを0.5時間反応させて感光性ポリイミドシロキサン溶液を得た。

【0047】（インキ化工程）上記の感光性ポリイミドシロキサンから実施例1と同様にして感光性ポリイミドシロキサン溶液組成物を調製し、評価を行った。この感光性ポリイミドシロキサン溶液組成物についての結果をまとめて表1および表2に示す。

【0048】また、露光・後加熱膜の機械的物性は、引張強度が $1.62\text{kg}/\text{cm}^2$ 、伸びが7.7%、初期弾性率が $55.5\text{kg}/\text{cm}^2$ であった。また、露光・後加熱膜の電気物性測定結果は体積抵抗値が $2.8 \times 10^{15}\Omega \cdot \text{cm}$ であった。この絶縁膜は、耐寒性も良好であった。

【0049】実施例3

（ポリイミドシロキサン合成工程）3, 3', 4, 4'-ベンゾフェノンテトラカルボン酸二無水物（BTDA）18.876gをN-メチル-2-ピロリドン54.0gに溶解し、ジアミノポリシロキサン（前記と同じ）36.540gを加え 180°C で2時間反応した。引き続き3, 3'-ジヒドロキシ-4, 4'-ジアミノビフェニル（HAB）3.765gを加え2時間反応した。次いで温度 100°C にて、グリシジルメタクリレート9.894gを加え0.5時間反応させて感光性ポリイミドシロキサン溶液を得た。

【0050】（インキ化工程）上記の感光性ポリイミドシロキサンから実施例1と同様にして感光性ポリイミドシロキサン溶液組成物を調製し、評価を行った。この感光性ポリイミドシロキサン溶液組成物についての結果をまとめて表1および表2に示す。

【0051】また、露光・後加熱膜の機械的物性は、引張強度が $1.12\text{kg}/\text{cm}^2$ 、伸びが6.5%、初期弾性率が $75.5\text{kg}/\text{cm}^2$ であった。また、露光・後加熱膜の電気物性測定結果は体積抵抗値が $1.8 \times 10^{15}\Omega \cdot \text{cm}$ であった。この絶縁膜は耐寒性も良好であった。

【0052】実施例4

実施例1において、タルクに代えてマイカを使用した他は同様の行って、感光性ポリイミドシロキサン溶液組成物を得た。結果は同じく良好であった。

【0053】比較例1

ジアミノシロキサンを使用しなかった以外は実施例1と同様にして、感光性ポリイミドシロキサンを得ようとしたが、ポリマーはN-メチルピロリドンに不溶であり、光硬化特性は測定できなかった。

【0054】比較例2

2, 3, 3', 4'-ビフェニルテトラカルボン酸二無水物に代えてピロメリット酸二無水物（PMDA）を使用した以外は実施例1と同様に実施して、感光性ポリイミドシロキサンを得た。得られた感光性ポリイミドシロ

【0057】 屈曲性を、島津製作所の折り曲げ試験器を用いて屈曲性を調べたところ、いずれも1mmφでもクランクが發生しなかった。半田耐熱性を、サリ化学製フラスコSF-270を表面に塗り、260℃の半田に30秒間浸漬して調べたところ、いずれも異常は認められなかった。耐無電解スズメッキ性を、シブレー製の無電解スズメッキ液（フジボットFT-34）に70℃で2分間浸漬して調べたところ、スズメッキ液のモグ

リイミッドアルム（宇部興産製、ユーレックス75S）に乾燥膜厚が30μmになるように塗布し、半田耐熱性と同様の条件で処理し、反りの發生を調べたところ、いずれにも実質的に認められなかった。反りを、市販の感光性ポリマーとして、太陽イソキ製の液状現象型ソルダレージストPSSR-100により、実施例5と同様にパターンニングを行った。その結果、1mmφの丸棒での屈曲テストでクラックが發生した。また、電気絶縁性は、初期値で1.2×10¹³Ω・cmであつた。

【表1】
【0059】

比較例3	a-BPDA	ジフェニノボリシロキサンの70	3, 5'-ジフェニノ安息香酸	30
比較例2	PMDA	ジフェニノボリシロキサンの70	3, 3'-ジヒドロキシ-4, 4'-ジフェニノビスフェニル	30
比較例1	a-BPDA	—	—	100
実施例3	BTDA	ジフェニノボリシロキサンの70	5, 5'-メチレンビス(2-フェニノ安息香酸)	30
実施例2	a-BPDA	ジフェニノボリシロキサンの70	3, 3'-ジヒドロキシ-4, 4'-ジフェニノビスフェニル	30
実施例1	a-BPDA	ジフェニノボリシロキサンの70	3, 3'-ジヒドロキシ-4, 4'-ジフェニノビスフェニル	30
酸二無水物の種類	ジフェニノ	ジフェニノ	ジフェニノ	

【0060】

【表2】

キサンはN-メチルピロリドンに溶解するのみであり、イソキ液は得られず光硬化特性は測定できなかった。

【0055】 比較例3
3, 3'-ジヒドロキシ-4, 4'-ジフェニノビスフェニルに代えて3, 5'-ジフェニノ安息香酸を使用した他は実施例1と同様に実施した。得られた感光性ポリイミドシロキサンはNMPに少ししか溶解せず、均一なイソキ液は得られず光感度は測定できなかった。

【0056】 実施例5～8

各実施例で得られた感光性ポリイミドシロキサン溶液組成物を、以下の方法でコート材を形成し、膜を評価した。厚さ75μmまたは50μmのポリイミドフィルム（ユーレックス-S）上に形成された銅回路パターン上にスクリーン印刷（200ミクロンメッシュ）により、イソキを塗布した。次いで60℃で1時間乾燥し有機溶媒を除去した。ミカサ（株）製のミカサマスコアライメント装置（MA-10型）を用いて、ガラスマスコアインの下で2分間超音波浸漬し、パターンの形成したメタノール中で2分間超音波浸漬し、絶縁膜を得た。次いで、160℃で1時間後加熱し、絶縁膜を得た。また、現像液として、1%のホウ酸ナトリウムとジエチレングリコールモノエーテルの20%水溶液を用いて行った以外は同様にして正常なパターンを得 *

表 1

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	対数粘度	製膜性	溶解性	熱分解温度 ℃	解像力 膜厚 μm	光感度 mJ/cm^2
実施例1	0.25	○	◎	416	26	80
実施例2	0.18	○	◎	408	25	50
実施例3	0.29	○	○	405	28	100
比較例1	—	—	×	—	—	—
比較例2	—	—	×	—	—	—
比較例3	—	—	△	—	—	—

【0061】実施例9

(ポリイミドシロキサン合成工程) a-BPDA34.94gをトリグリム100gに溶解し、ジアミノポリシロキサン (R_1 =プロピル、 R_2 =メチル、アミノ当量=467) 65.006gを加え、180℃で1時間反応させた。引き続いて同温度でMBAA12.250g加え20時間反応し、次いで温度100℃にて所定量のグリシジルメタクリレート (酸成分:ジアミン成分=1.00:1.00)を加え0.5時間反応させて感光性ポリイミドシロキサンを得た (溶液として)。

【0062】(インキ化工程) 上記感光性ポリイミドシロキサン溶液である重合液 (固形分濃度53.7%) 100部 (重量部、以下同じ) に対して、フタロシアニングリーン0.268部を加え分散させ、その溶液にハーブエポキシアクリレート (昭和化学工業社製、商品名:リポキシ630X-501) 14.42部、ポリエチレングリコールジメタクリレート (新中村化学工業社製、NK9G) 5.37部、ジメタクリロイルオキシフオスフェートとモノメタクリロイルオキシフオスフェートとの1:1の混合物であるリン酸メタクリレート (日本化薬工業社製、PM2) 1.61部を加え、続いて消泡剤 (ダウケミカル社製、DB100) 2.74部、開始剤 (チバガイギー社製、イルガキュア184) 14.67部、開始剤 (チバガイギー社製、イルガキュア369) 7.33部、ジメチルアミノ安息香酸エチルエステル5.87部、ジエチルチオキサントン2.93部、ゲル化防止剤としてハイドロキノン0.27部、およびメトキシハイドロキノン0.27部、次に、硫酸バリウム (平均粒子径:0.3 μm) 16.1部とアエロジル (平均粒径:約0.02 μm) 5.37部を加え、3本ロールで混練してインキ:感光性ポリイミドシロキサン組成物を得た。

【0063】このインキから常法通りにコート材を形成し、耐無電解錫メッキ性を無電解錫メッキ液 (シプレー社製、テンポジットFT-34) に70℃で3分間浸漬

して確認したところ、錫メッキ液のもぐりは実質的に認められなかった。また、このインキを厚み35 μm の銅箔に塗布し、60℃で60分間乾燥し、乾燥膜厚が23 μm でミカサ社製のミカサマスクアライメント装置を使用して100 mJ/cm^2 の光感度で露光した後、テトラエチルアンモニウムハイドロオキシサイドの2%水溶液およびメタノール中で超音波浸漬して現像し、100 μm ライン&スペースのパターンを得ることができた。この露光・後加熱膜は実施例1と同等の良好な機械的・熱的 (含耐寒性、以下同じ)・電気的物性を示した。

【0064】実施例10

(インキ化工程) 実施例9と同様にして得られた感光性ポリイミドシロキサン溶液である重合液 (固形分濃度53.7%) に、リン酸メタアクリレートに代えてメラミン樹脂 (サンワケミカル社製、ニカラックMW-100LM) 16.1部を加えた他は実施例9と同様に実施して、インキ:感光性ポリイミドシロキサン組成物を得た。

【0065】このインキから常法通りにコート材を形成し、耐無電解錫メッキ性を無電解錫メッキ液 (シプレー社製、テンポジットFT-34) に70℃で3分間浸漬して確認したところ、錫メッキ液のもぐりは実質的に認められなかった。また、このインキを厚み35 μm の銅箔に塗布し、60℃で60分間乾燥し、乾燥膜厚が23 μm でミカサ社製のミカサマスクアライメント装置を使用して100 mJ/cm^2 の光感度で露光した後、テトラエチルアンモニウムハイドロオキシサイドの2%水溶液およびメタノール中で超音波浸漬して現像し、100 μm ライン&スペースのパターンを得ることができた。この露光・後加熱膜は実施例1と同等の良好な機械的・熱的・電気的物性を示した。

【0066】実施例11

(インキ化工程) リン酸メタアクリレートを加えず、硫酸バリウム16.1部に代えて炭酸カルシウム (平均粒子径:1.2 μm) 16.1部を使用した他は実施例9

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出口

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七 日

2004